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Lithium/Polymer Electrolyte Interfacial Instability

by

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# LITHIUM/POLYMER ELECTROLYTE INTERFACIAL INSTABILITY

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## ABSTRACT

The stability of evaporated lithium with poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO) and oxyethylene-oxyethylene copolymer, doped with lithium perchlorate, in ultra-thin-film cells, was studied by impedance spectroscopy at room temperature. The formation and growth of a passivating film at the lithium/PEO interface has been observed, under open circuit conditions. The thickness of the passivating layer was estimated by assuming the dielectric constant of the interfacial product. A more extensive interfacial reaction was observed in the case of PPO. A very fast interfacial reaction was observed between lithium and amorphous copolymer

**Keywords:** interface, thin film cell, polymer electrolyte



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## INTRODUCTION

The formation of a passivating layer at the electrode-electrolyte interface has been reported as occurring in many electrochemical cells containing liquid electrolytes in contact with highly reactive electrodes such as lithium metal. The presence of such a layer considerably reduces the apparent exchange current density [1]. Two types of passivating film have been proposed: a compact solid electrolyte interface (SEI)[2] and a porous polymer electrolyte interface (PEI)[3]. In the first case the observed exchange current density is reduced because of the additional non-ohmic series resistance of the layer, whereas in the second, partial coverage of the interface reduces the effective area perpendicular to the current path.

Since the original proposal that poly(ethylene oxide) (PEO) doped with alkali metal salts could be used as an alternative to liquid electrolytes [4], many other polyether electrolytes have been characterized. Many studies of cell performances have been made, and today the PEO-LiX solid electrolytes may be regarded as one of the most promising developments in modern battery technology [5].

The main thrust of recent work on polymer electrolytes for lithium batteries has been towards the synthesis and characterisation of highly conducting material. However, little attention has been paid to the stability of these electrolytes when in contact with lithium electrodes. The cyclability of the lithium electrode depends on the nature

of the electrolyte. Studies on relatively thick cells (100-300  $\mu\text{m}$ ) of PEO - lithium salts with pressed lithium electrodes, operated above room temperature, revealed the presence of a passivating layer at the lithium/polymer interface [6,7], and this could seriously affect the performance of the cell. The resistance of the reaction products at the interface may well be the factor which limits performance, especially in very thin cells [8].

The present work was intended to evaluate the effects of interfacial reactions at room temperature between polymer electrolytes and evaporated lithium electrodes in very thin film (4  $\mu\text{m}$ ) cells. This configuration is particularly sensitive to interfacial restrictions, since potential drops due to the bulk electrolyte are smaller. In this case the electrode/electrolyte contact is better defined and also the results are relevant to a possibly important technology in which evaporated lithium, rather than foil, is used. The studies were directed at identifying the nature of the layer as well as the kinetics of the corrosion process which causes the layer to increase its thickness with time. Because of the difficulties in the application of electron microscopy to the extremely air-sensitive samples, a method was developed for extracting information concerning the interfacial layer, from impedance data.

## EXPERIMENTAL

### i. Preparation of polymers:-

The following polymer electrolytes were prepared for the

evaluation of their stability with evaporated lithium:-

- a. PEO-LiClO<sub>4</sub> (x = 8) (partially crystalline)
- b. PPO-LiClO<sub>4</sub> (x = 8) (amorphous)
- c. Oxyethylene-oxyethylene copolymer  
with LiClO<sub>4</sub> (x = 8) (amorphous)

where  $x = [\text{EO units}]/[\text{Li}]$

PEO of molecular weight 5,000,000, supplied by Aldrich, was dried under partial vacuum at 50°C. Lithium perchlorate trihydrate supplied by BDH was dried under partial vacuum at 100-110°C for about 48 h. A 4 % solution of PEO-LiClO<sub>4</sub> ([EO units]/[Li] = 8) was prepared by dissolving preweighed PEO and LiClO<sub>4</sub> in acetonitrile.

By dissolving appropriate amounts of poly(propylene oxide) (PPO), supplied by Hercules Inc. (under the trade name of Parel 58), and dry LiClO<sub>4</sub> in acetonitrile, a 4 % solution of PPO-LiClO<sub>4</sub> ([EO units]/[Li] = 8) was prepared

The oxyethylene-oxyethylene copolymer (supplied by Dr.C. Booth, Manchester University) was of the type  $[(\text{OCH}_2\text{CH}_2)_n\text{OCH}_2]_m$  where n is about 9 and m > 500. The copolymer was dissolved in THF to make an approximately 3 % solution again containing one LiClO<sub>4</sub> per eight ether oxygens. The preparation of the undoped polymer is described elsewhere [9].

#### 11). Sample preparation:-

The cell configuration used for most of these experiments was Ni/polymer electrolyte/Li. In this case the absence of

an electronic short circuit could easily be confirmed by a zero steady state current on application of a positive potential to the nickel electrode.

Nickel tracks were evaporated onto the clean glass substrates through an appropriate mask (fig.1a), using a standard vacuum evaporator. All further fabrication and measurements were done under an argon atmosphere in a dry box. A solution of polymer in acetonitrile was applied across the contacts by dip coating using PTFE tape as a mask. The solvent was evaporated leaving a thin polymer film (fig.1b). The polymer film was transferred to a vacuum evaporator housed within the dry box and left to dry for about 16 h under a vacuum of  $4 \times 10^{-5}$  torr. The lithium electrode was made by vacuum evaporation, through another mask, across the polymer film making a bridge to the nickel track (fig.1c). The substrate to source distance was 14 cm during the lithium evaporation. Different thicknesses of lithium were applied during the fabrication of different arrays by evaporating lithium foils of different weight. During one such operation an array of eleven cells, each having an effective area of  $0.08 \text{ cm}^2$ , was fabricated on a single substrate.

Cells having a Ni/polymer electrolyte/Ni structure were prepared by coating nickel in place of lithium at the last stage.

#### 111). Measurements:-

Complex impedance measurements were made through the nickel

contacts, on all the cells, in the frequency range 13 MHz to 5 Hz at room temperature using an HP 4192A LF Impedance Analyser. The amplitude of the oscillator signal was 100 mv RMS. Impedance measurements were also taken of the co-axial leads connecting the cells to the analyser with the cell end open and shorted alternately. The complex impedance measurements were repeated at various time intervals after the initial fabrication.

The electrolyte thickness was difficult to measure directly but S.E.M. observations of selected samples showed a variation across the array between 2 and 4  $\mu\text{m}$ .

## THEORY

In this section we show how the frequency spectrum of the complex impedance may be used to elucidate the structure of the interfacial layer.

The typical impedance spectrum of a sample containing two phases in electrical series consists of two semicircles in the complex plane plot, e.g. fig.2. Each phase is identified with one semicircle whose diameter signifies the resistance contribution of that phase. Which semicircle belongs to which phase can be decided as follows.

The reciprocal of the impedance, i.e. admittance, is given by

$$Y^* = 1/Z^* = 1/R + j\omega C = A/l(\sigma + j\omega\epsilon_0\epsilon_r) \quad \dots(1)$$



where C is the capacitance  
 R is the resistance  
 $\sigma$  is the conductivity  
 $\epsilon_r$  is the dielectric constant  
 $l$  is the thickness  
 A is the cross-sectional area.  
 $\epsilon_0$  is the permittivity of free space and  
 $\omega$  is the measuring angular frequency

In each semicircle the imaginary part of the impedance reaches a maximum value when real and imaginary parts of the impedance (or admittance) are equal, i.e. when the angular frequency

$$\omega^* = 1/RC \quad \dots(2)$$

The value of  $\omega^*$  is geometry-independent because:

$$R = l/\sigma A \quad \text{and} \quad C = A \epsilon_0 \epsilon_r / l$$

$$\text{so that } \omega^* = \sigma/\epsilon_0 \epsilon_r \quad \dots(3)$$

This shows that  $\omega^*$  is a fundamental property of the single phase from which it may be identified. If neither the thickness nor the conductivity of the phase concerned is unknown, use can still be made of the  $\omega^*$  value by assuming a value of about 10 for the dielectric constant. In the absence of ferroelectric effects this is considered a reasonable assumption to within one order of magnitude at

least. Accordingly, the thickness and conductivity of the phase are given by:

$$\lambda = \omega^* \epsilon_0 \epsilon_r A R \quad \dots(4)$$

$$\sigma = \omega^* \epsilon_0 \epsilon_r \quad \dots(5)$$

The above theory should apply to the compact (SEI) layer interfacial phase as well as the polymer electrolyte.

Now we shall consider the porous (PEI) case. The interface is now composed of two ionic conductors in parallel. The admittance of the combination is:

$$Y^* = (1/\lambda) \{A_1 \sigma_1 + A_2 \sigma_2 + j\omega \epsilon_0 (A_1 \sigma_1 + A_2 \sigma_2)\} \dots(6)$$

Comparison with equations (1) and (3) shows that:

$$\omega^* = \{A_1 \sigma_1 + A_2 \sigma_2\} / \epsilon_0 \{A_1 \sigma_1 + A_2 \sigma_2\} \quad \dots(7)$$

$\omega^*$  is now formed from area-weighted averages of conductivity and dielectric constants of the two materials, and varies between the values corresponding to the pure phases according to the area fraction. If we now assume equal dielectric constants for the two phases equation (4) still applies, and (5) gives the area-weighted average of the two conductivities.

## RESULTS AND DISCUSSION

For all the impedance measurements, a lead correction was applied as mentioned previously [10]. Fig.2 shows the impedance plot obtained for a Ni/PEO-LiClO<sub>4</sub>/Li cell in which the lithium electrode was coated by evaporating 0.4 g of lithium. It is evident that there are two distinct relaxation phenomena in this system, with  $R_1 = 2.5 \text{ k}\Omega$ ,  $\omega_1^* = 2\pi \times .160 \text{ krad.s}^{-1}$  and  $R_2 = 5.7 \text{ k}\Omega$ ,  $\omega_2^* = 2\pi \times .60 \text{ rad.s}^{-1}$  respectively.

According to equation (4), the first relaxation corresponds to a phase of thickness  $1.8 \text{ }\mu\text{m}$  assuming a dielectric constant of 10, and is therefore assigned to the PEO. This agrees reasonably well with SEM observations of PEO layers deposited in a similar way. (The assignment is confirmed by fig.3 which shows the complex impedance plot of a Ni/PEO-LiClO<sub>4</sub>/Ni cell. Only one relaxation can be observed, corresponding to PEO with  $\omega^* = 2\pi \times .160 \text{ krad.s}^{-1}$  ) Across a number of cell arrays the PEO thickness calculated in this way varied from  $1.8 \times 10^{-4}$  to  $3.6 \times 10^{-4} \text{ cm}$ . The conductivity remained constant at about  $10^{-6} \text{ }\Omega^{-1}.\text{cm}^{-1}$ . The lowest resistance-area product obtained was  $160 \text{ }\Omega.\text{cm}^2$ ; attempts at constructing cells with thinner electrolytes resulted in short circuit failure.

The second relaxation, (Fig.4) showed a resistance increasing monotonically with time. This result is interpreted as being due to an interfacial reaction layer as previously observed by Fauteux (6). We also note a constant

$\omega^*$  value, indicating that the layer conductivity of about  $10^{-10} \Omega^{-1}\text{cm}^{-1}$  is constant and that the increasing resistance is due to increasing thickness, as in the SEI model. Again assuming a dielectric constant of 10, we can calculate that, 35 min after the cell fabrication, the thickness is 16 Å.

Fig.5 shows the complex impedance spectrum of a Ni/PEO-LiClO<sub>4</sub>/Li cell formed by evaporation of only 0.2 g of lithium foil, so that the thickness of the lithium electrode was about half that in the previous case. The interfacial resistance of this cell is much higher than that of the previous one (fig.2), but the  $\omega^*$  value is similar. This large increase in the interfacial resistance with the thickness of the lithium electrode may be explained by incomplete coverage of a rough polymer surface by the very thin lithium. The roughness of the polymer surface is estimated to be of the order of 1  $\mu\text{m}$  from S.E.M. observations - a similar value for the thickness of lithium can be expected from a 0.2g charge at a distance of 14 cm and a sticking coefficient of 0.3.

Fig.6 shows the complex impedance plot of a typical Ni/PPO-LiClO<sub>4</sub>/Ni cell. These cells showed consistent values of cell resistance and  $\omega^*$  values, although the cell resistances were much higher and  $\omega^*$  much lower than those of PEO cells. In this case equation (4) gave unreasonably large values of thickness if  $r = 10$  was assumed; a value of 2, however, gave the expected thickness of 2  $\mu\text{m}$ . Accordingly, the conductivity was found to be about  $10^{-8}$

$\Omega^{-1}\text{cm}^{-1}$  using  $\sigma = 1 / RA$ . Cells with a lithium electrode were found to be far less reproducible, with only a few showing semicircles and most showing open or short circuit failure. In the cases where impedance diagrams could be analysed, only one semicircle could be seen, e.g. fig.7. A tentative analysis in this case gives a thickness of  $1\text{ }\mu\text{m}$  and a conductivity of about  $10^{-9}\text{ }\Omega^{-1}\text{cm}^{-1}$ . A variation of both resistance and  $\omega^*$  values from one cell to the next may be explained by a thick, porous phase according to equation (6). However, gross deterioration of either the lithium electrode contact is equally plausible. Either way, compared to PEO there was a far more extensive interfacial reaction, which may well have been due to impurities in the PPO rather than to the polymer itself.

An even more dramatic failure was observed with the amorphous copolymer. Soon after lithium was evaporated on the polymer and removed from the evaporator, most of the lithium film had reacted with the polymer, leaving only a few patches of lithium on the polymer.

## CONCLUSIONS

Ultra-thin PEO cells have been constructed with resistance-area products, due to the electrolyte, as low as  $160\text{ }\Omega.\text{cm}^2$  without short circuit failure. However, the overall resistance of such cells was raised to more than  $1\text{ k}.\text{cm}^{-2}$  by a compact interfacial reaction product a few nanometres thick with a conductivity of about  $10^{-10}\text{ }\Omega^{-1}\text{cm}^{-1}$ .

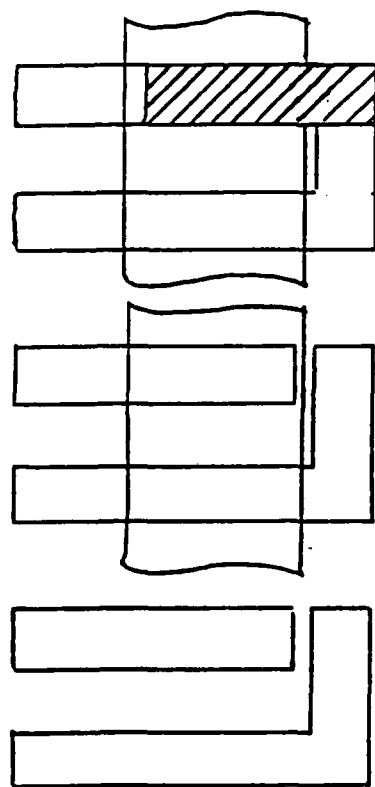
Interfacial reactions between lithium and some amorphous electrolytes were far more severe, and generally led to cell failure.

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(a)

(b)

(c)

Fig.1. Cell fabrication steps



Fig.2. Impedance spectrum of a Ni/PEO/Li cell (thick lithium layer)

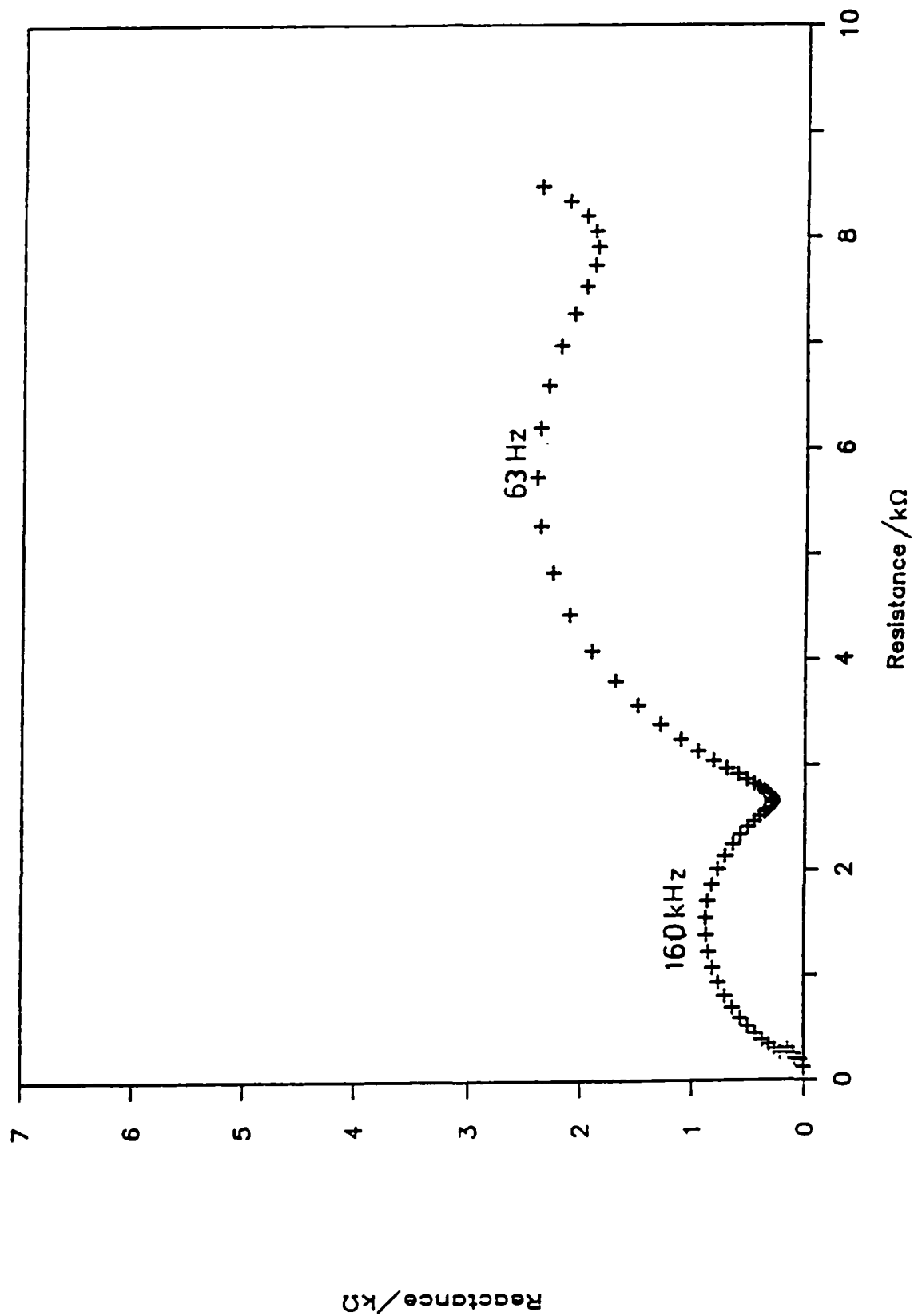


Fig.3. Impedance spectrum of a Ni/PEO/Ni cell

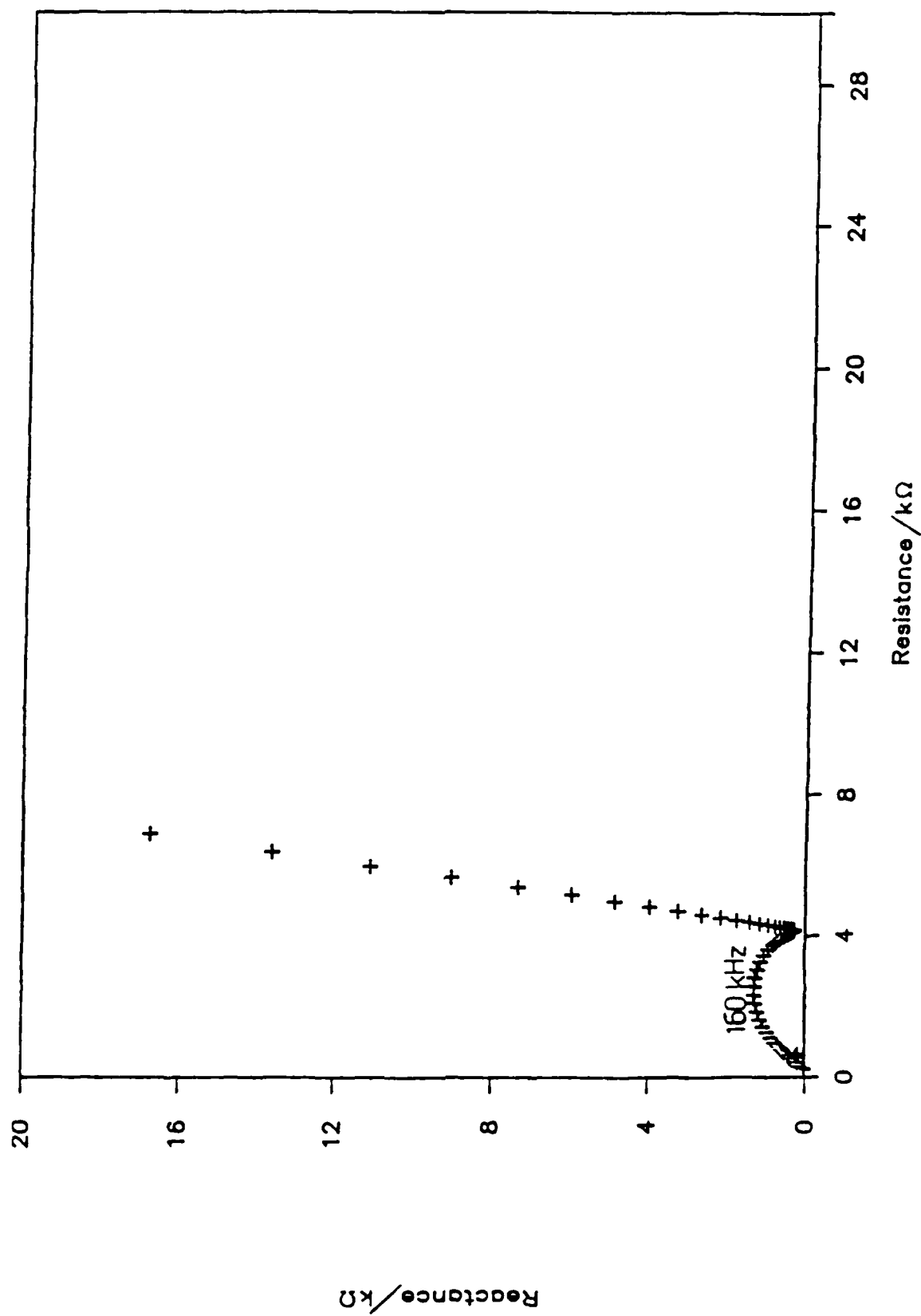


Fig.4. Plot of interfacial resistance  $R_i$  versus time

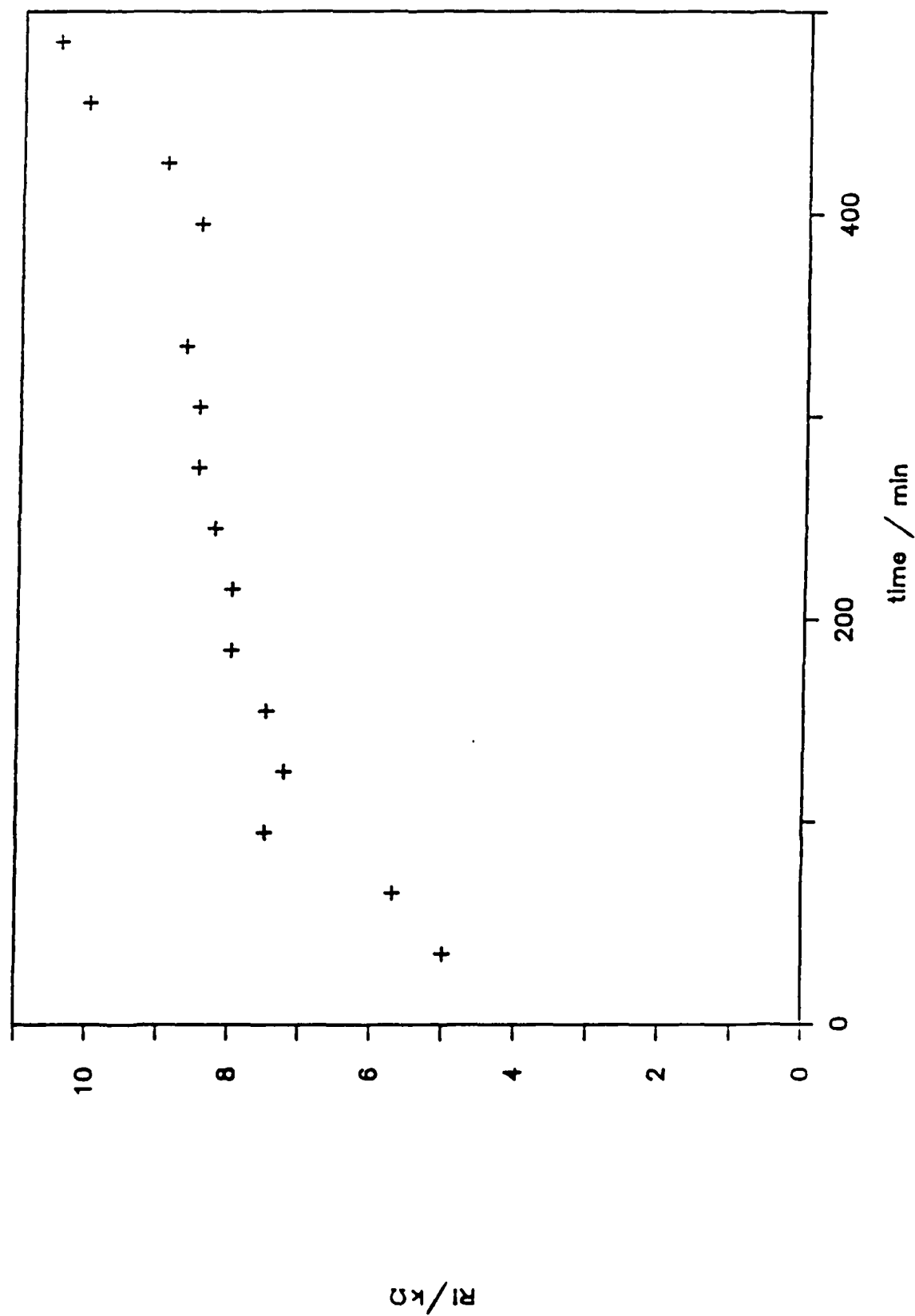


Fig.5. Impedance spectrum of a Ni/PEO/Li cell (thin lithium layer)

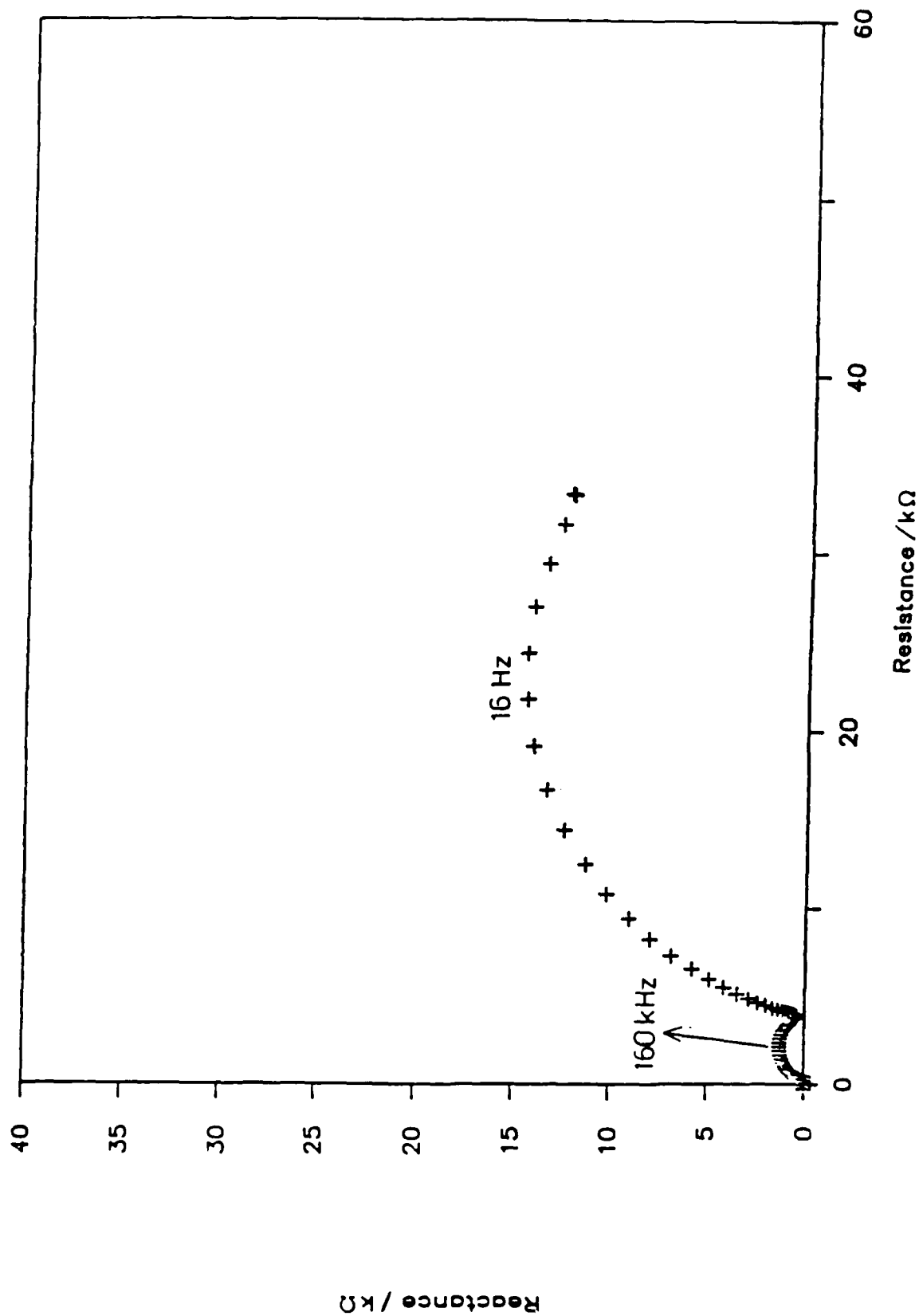


Fig.6. Impedance spectrum of Ni/PPO/Ni cell

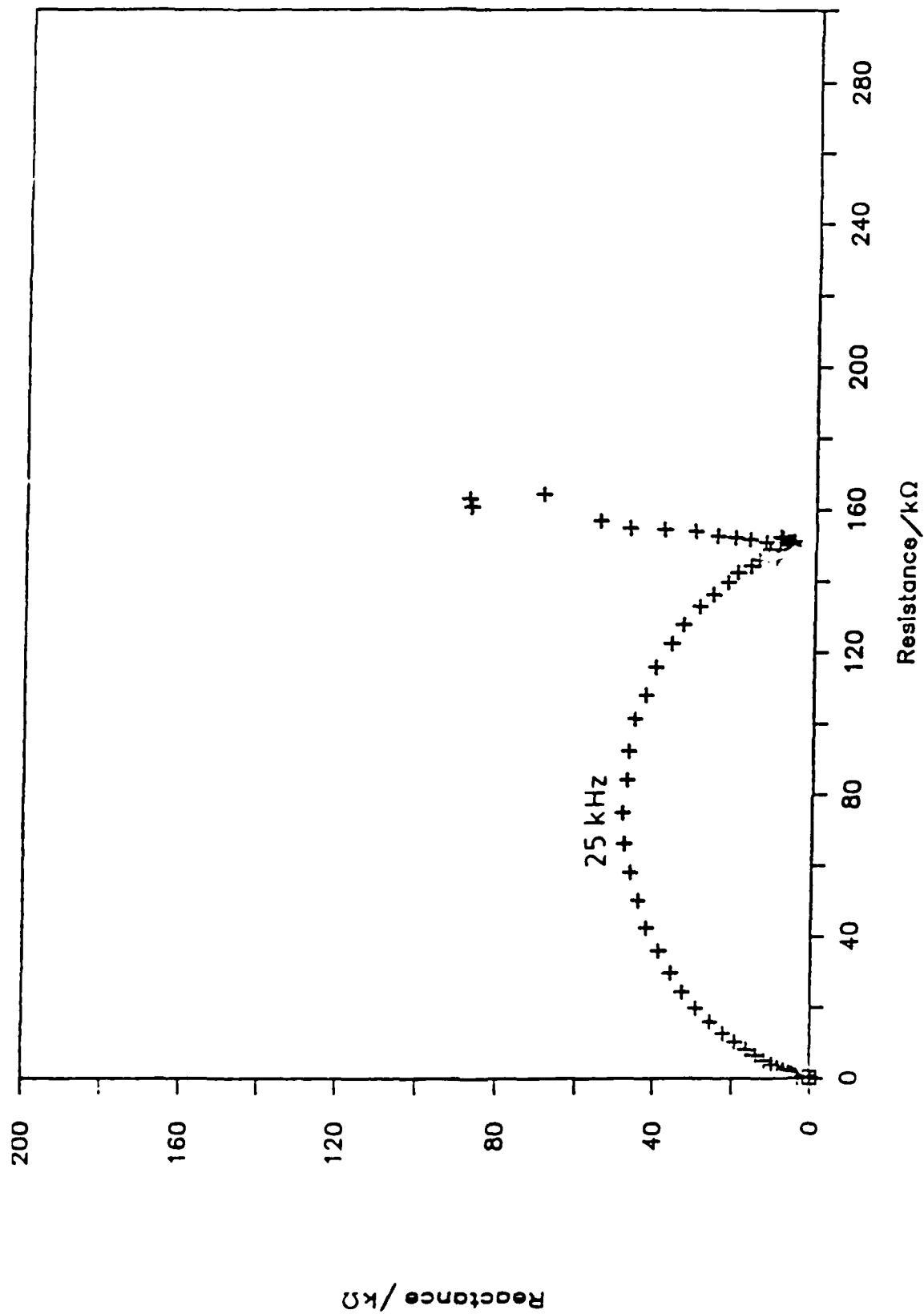


Fig.7. Impedance spectrum of a Ni/PPO/Li cell

